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ABSTRACT

Description of a method for coating graphite with titanium and zirconium carbides by soaking graphite in liquid metal with subsequent carbidization of the metallic layer. Values for microhardness, lattice period and carbon content in titanium and zirconium carbides, obtained under conditions of annealing, are tabulated. The effect of porosity on the quality of carbide coatings is also considered.

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The wide use of graphite as a highly refractory metal with great strength at high temperatures is considerably restricted by the fact that this material is rather strongly oxidized and pitted, as well as eroded in high velocity gas streams. Various methods are used for applying coatings of refractory metals and compounds of these metals to graphite as a protective measure. Some interesting methods for applying these coatings to graphite are described in the literature. For instance, data are given in reference 1 on the application of glass-carbon-silicide coatings to carbon and graphite materials for protecting them from oxidation at temperatures up to 1200°C. An interesting method is described in reference 2 for application of zirconium,

*Numbers given in the margin indicate pagination in original foreign text.

niobium and titanium carbide by dissociation of chloride vapors, producing the free metal together with its oxide.

In the present work, we studied conditions for the application of titanium and zirconium carbide coatings to graphite by soaking the material in the molten metal and then converting the metal layer to its carbide. Graphite with various degrees of porosity (grades A, B and C) was studied. Plates were cut from the graphite with dimensions of 20 × 30 × 3-5 mm. The surfaces of these plates were then roughened by sanding and placed in a graphite holding device with a double bottom. The specimens were covered with metal powder calculated at 0.3 grams per square centimeter of surface. The holder was placed in a vacuum resistance furnace with a graphite heater and heated to a temperature 50-100° above the melting point of the metal (residual pressure in the furnace was 10^{-4} mm Hg, holding time was 20-30 minutes).

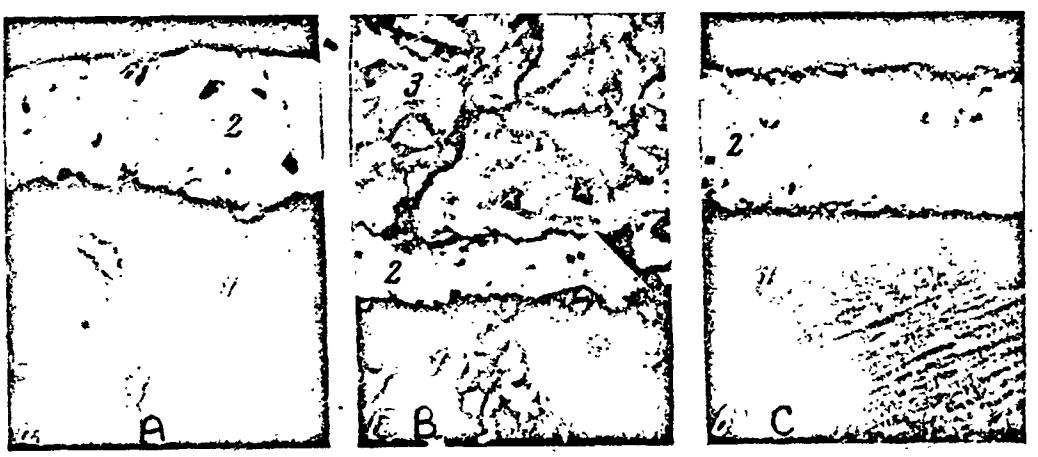

Fig. 1. Microstructures of graphite specimens coated with titanium: *a*--metal layer of titanium on graphite; *b*--partially carbidized titanium layer; *c*--completely carbidized coating; (*1*--graphite; *2*--titanium carbide; *3*--solid solution of carbon in titanium) (340×).

As the metal was melted, the specimen of graphite was covered with a uniform layer. The excess metal was drained off through a small opening in the lower cavity of the holding device. The sample was then annealed, converting the metal coating to its carbide through diffusion.

The constants for diffusion of carbon into metals (reference 3) may be used for calculating the time necessary for conversion of the metal layer into a single-phase carbide layer at a given annealing temperature. Repeated application may be used for controlling the thickness of the layer.

Thin sections were taken from the coated graphite specimens for /148 studying the microstructure and for measuring the microhardness throughout the width of the layer. The coatings were subjected to X-ray analysis to ascertain whether the carbide phase was present and to determine its lattice constant. The composition of the carbide phase was determined by chemical analysis.

The structure of a graphite specimen immediately after coating with metallic titanium is shown in figure 1*a*. It can be seen that the interface is

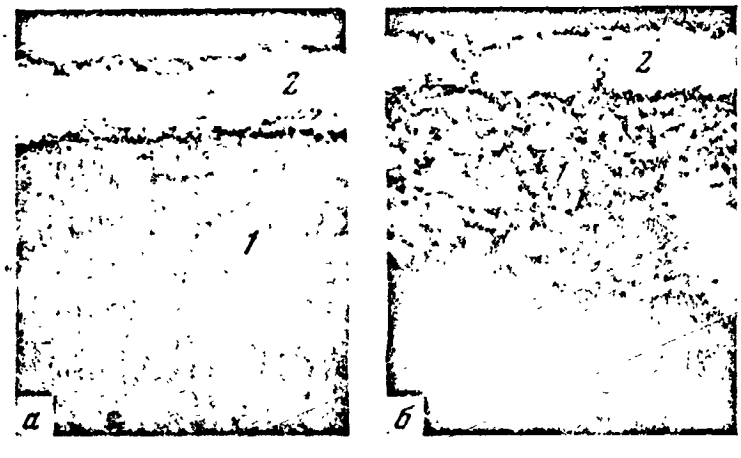

Fig. 2. Microstructures of graphite specimens with zirconium carbide coatings: *1*--graphite; *2*--zirconium carbide (340×).

friable and that the layer is held mainly by mechanical bonding. A new phase is formed at the graphite—metal interface by diffusion annealing of the coated specimen for 1 hour at 1500°C (figure 1*b*). Measurements of the microhardness of the coatings show that this new phase is titanium carbide, the outer layer being a solid solution of carbon in titanium. Increasing the annealing time to 2 hours results in complete conversion of the metal layer to its carbide. The lattice constant of the titanium carbide which is formed (figure 1*c*) is 4.307 angstroms.

Data given in reference 4 on the relationship between the lattice constant of titanium carbide and its carbon content show that this titanium carbide is far from stoichiometric (∿11 wt.% C). Chemical analysis of the coating confirmed these data. When the diffusion annealing temperature is increased, the lattice constant of the TiC also increases because of the higher carbon content.

TABLE 1

Annealing temperature °C	*a* Angstroms	H_μ, kg/mm^2 (50 gram load)	C, wt.%
1500	4.301	2813	11.00
1600	4.312	2902	16.90
1700	5.319	3144	20.01

TABLE 2

Annealing temperature °C	*a* Angstroms	H_μ, kg/mm^2 (50 gram load)	C, wt.%
1600	4.645	2400	8.0
1700	4.666	2630	9.8
1800	4.688	2750	11.6

Data are given in table 1 on the microhardness and lattice constant of titanium carbide and the concentration of carbon in the coatings as a function of diffusion annealing temperature with a two hour holding period. Chemical analysis shows a carbon content of 20.01% in a specimen with a lattice constant of 4.319 angstroms, which corresponds to stoichiometric TiC.

The same method was used for applying zirconium carbide coatings to graphite. The graphite was covered with metallic zirconium at 1950°C, and the specimen was then subjected to diffusion annealing at a lower temperature.

Table 2 gives the microhardness, lattice constant and carbon content for zirconium carbide coatings as a function of temperature with a two hour diffusion annealing.

A solid coating of single-phase zirconium carbide up to 50 μ /149 thick can be produced by further annealing at 1800°C for two hours. This coating has a composition close to stoichiometric ZrC.

Tables 3 and 4 show the results of calculations for the lattice constants of carbide coatings on graphite produced under optimum conditions.

TABLE 3
(a = 4.321 angstroms)
CALCULATIONS OF THE LATTICE CONSTANT OF TITANIUM CARBIDE

No	I	d/n	hkl
1	V. s.	2.4940	111
2	V. s.	2.1610	200
3	V. s.	1.5270	220
4	V. s.	1.3040	311
5	S.	—	—
6	M.	1.2500	222
7	S.	0.9943	—
8	V. s.	0.9683	420
9	V. s.	0.8848	422

TABLE 4
(a = 4.628 angstroms)
CALCULATIONS OF THE LATTICE CONSTANT OF ZIRCONIUM CARBIDE

No	I	d/n	hkl
1	V. s.	2.7140	111
2	V. s.	2.3490	200
3	V. s.	1.6580	220
4	V. s.	1.4170	311
5	S.	1.3600	222
6	W.	1.1590	400
7	S.	1.0740	331
8	S.	1.0470	420
9	S.	0.9574	422
10	S.	0.9031	333
11	M.	0.8284	440

The effect of porosity on the quality of carbide coatings was studied. It was found that the densest coatings and those most tightly bound to the substrate are produced when the porosity of the graphite is at a minimum.

A new method is proposed in reference 5 for making titanium carbide parts by casting molten titanium in special graphite molds filled with graphite grit and then annealing the cast parts. It was found that annealing time and temperature affect the composition of the resulting carbide in a manner similar to that observed in the present work.

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